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ETHANOL FROM CELLULOSIC RESIDUES AND CROPS

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ABSTRACT

The Tennessee Valley Authority, in cooperation with the U.S. Department of Energy (DOE) and the Solar Energy Research Institute (SERI), is developing concentrated acid hydrolysis technology for producing fuel-grade ethanol from agricultural cellulosic materials. The low-temperature, low-pressure, concentrated acid hydrolysis process developed by TVA has been evaluated in a 4-t/d-of-feedstock experimental facility (1984 to 1986) using corn stover feedstock. Hemicellulose and cellulose conversion efficiencies over 90 percent were achieved. Several process optimization and acid recovery studies are being conducted to decrease acid requirements and improve the overall efficiency of the process. Hydrolysis processing options evaluated and discussed in this paper include hydrolyzate recycle, high-pressure pressing, high-intensity mixing, and microwave and radio-frequency drying. Acid recovery research results are given in the areas of adsorption, solvent extraction, and ion exchange.

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INTRODUCTION

The Tennessee Valley Authority (TVA), in cooperation with the U.S. Department of Energy (DOE) and the Solar Energy Research Institute (SERI), is developing technology for producing fuel-grade ethanol from agricultural cellulosic materials. Laboratory and bench-scale research to define a low-temperature, concentrated sulfuric acid hydrolysis process began in 1983. The process selected by TVA is based on the sulfuric acid hydrolysis process developed at the U.S. Department of Agriculture's (USDA) Peoria Laboratory (Dunning and Lathrop 1945, 1948). Several variations of the Peoria process have been evaluated at Purdue University, the University of Missouri, the University of Arkansas, and the University of California-Berkeley. Based on the results of these earlier studies and TVA's bench-scale work, a 4-t/d-of-feedstock experimental facility was constructed in 1984 (Barrier, et al., 1985).

Process evaluations conducted in the facility using corn stover (1984-1986) resulted in hemicellulose and cellulose conversion efficiencies in excess of 90 percent (Barrier, et al., 1986). Since 1986, laboratory- and bench-scale tests have been conducted to optimize the concentrated acid hydrolysis process.

The objectives of the TVA/DOE/SERI project are to: (1) develop commercially acceptable process technology for producing fuel ethanol from cellulosic residues and crops using the TVA/DOE experimental facility, (2) assess and develop process and equipment options in laboratory- and bench-scale tests prior to engineering development in the experimental plant, (3) evaluate the technical and economic feasibility of all components of an integrated fuel ethanol production system (i.e., feedstock options; conversion processes; recovery of products and coproducts; waste treatment, disposal and utilization; and product handling and storage), and (4) develop effective mechanisms for transfer of commercially feasible technology to private industry.

This paper describes the results of acid hydrolysis and acid recovery research conducted during fiscal year 1987, designed to increase the overall efficiency of the concentrated sulfuric acid hydrolysis process.

EXPERIMENTAL DESIGN

Acid hydrolysis process optimization research has focused on the development of processing options to improve materials handling, increase sugar concentrations, decrease acid requirements, and allow for semibatch process operation. Hydrolysis process options evaluated in the laboratory include: (1) recycle of first-stage hydrolyzate to increase sugar

concentrations, (2) high-pressure pressing for more efficient liquid/solids separation, (3) high-intensity mixing for better dispersion of acid throughout the feedstock, and (4) microwave- and radio-frequency-assisted vacuum drying to decrease drying time.

Acid recovery research is being conducted to determine the potential of using either solvent adsorption, extraction, and ion exchange technology for the recovery of sulfuric acid in the TVA process. The adsorption process involves adsorption of sugars from a sugar/acid hydrolyzate onto activated charcoal, followed by desorption of the sugars using hot ethanol. The sugars crystallize upon cooling of the ethanol. The solvent extraction process involves extraction to recover the sulfuric acid followed by a second extraction and distillation to recover the solvents. Using ion exchange technology, commercially-available resins are being used to determine their potential in recovering sulfuric acid.

RESULTS

Acid Hydrolysis Research

Recycling of Hydrolyzates--Corn stover was hydrolyzed in 10-percent sulfuric acid for 2 hours. A 10-percent acid concentration was used so that multiple recycling would not dilute the acid below the minimum effective hydrolysis concentration of 4 to 5 percent. The solids were separated by filtration, and the liquid product was recycled. Four first-stage hydrolysis cycles were conducted using fresh stover and recycled hydrolyzate. Table 1 shows the experimental xylose and acid concentrations as compared to those predicted by a computer model. The xylose and acid concentrations compared favorably with those predicted by the model. Analysis of the hydrolyzate showed negligible degradation of xylose to furfural (Lightsey 1985).

Table 1

Comparison of Experimental and Predicated Values During
Acid Reuse in First-Stage Hydrolysis

<u>Cycle No.</u>	<u>Acid Concentration (%)</u>		<u>Xylose Concentration (%)</u>	
	<u>Predicted</u>	<u>Measured</u>	<u>Predicted</u>	<u>Measured</u>
Initial	-	10	-	-
1	6.7	6.5	3.1	2.8
2	6.5	6.3	5.4	5.0
3	6.3	6.0	7.1	6.5
4	6.2	6.0	8.4	7.8

Dewatering and Mixing--Dewatering of the solids from the hemicellulose hydrolysis step was conducted in the laboratory using a plate-type hydraulic press. The pressed solids from this step contained approximately 35- to

40-percent moisture. Ribbon- and screw-type mixers were then used to mix the solids with sulfuric acid ranging in concentration from 25 to 50 percent at 2:1, 4:1, and 6:1 liquid-to-solids ratios. Mixing at 2:1 and 4:1 liquid-to-solids ratios gave poor results with visible dry spots. Mixing at a liquid-to-solids ratio of 6:1 gave excellent results using both types of mixing equipment. The slurries were then dewatered using the hydraulic press. Pressing of the slurries mixed with 40- and 50-percent acid resulted in residues with a solids content of only 25 to 30 percent. Pressing of the slurries mixed with less than 35-percent acid resulted in residues with solids contents of 60 to 65 percent (Lightsey and Bharat 1987).

Drying--The rate of drying of acid-impregnated corn stover was evaluated using conventional vacuum drying and microwave- and radio-frequency-assisted drying (vacuum and atmospheric). In each drying experiment, a preweighed amount of wet solids (about 60 g with 30 percent acid) was placed in a dish so that the solid thickness was approximately 2 cm. The samples were removed from the drying ovens at various times and weighed until the moisture loss equaled the amount calculated to give 80 percent acid in the aqueous phase. The results of these tests are shown in Figure 1.

Laboratory tests involving conventional vacuum drying were conducted using an oven at 80°C and 25 in.Hg vacuum. After approximately 4 hours, the acid concentration in the aqueous phase had reached the desired level. Drying of solids using microwave energy in both atmospheric and vacuum ovens was rapid (from 4 to 6 minutes). Process control was difficult due to the rapid heating rate. Charring of solids resulted in some instances. Vendor tests using cooling air kept the temperature below the decomposition level. Radio-frequency (RF) drying experiments were conducted using both ambient and dessicated air and various RF discharge openings. Drying times were from 8 to 20 minutes. The use of dessicated air and/or greater RF power significantly increased the drying rate. The use of ambient air caused the solids to char. No significant degradation was found in the samples dried with dessicated air (Lightsey, et al., 1987).

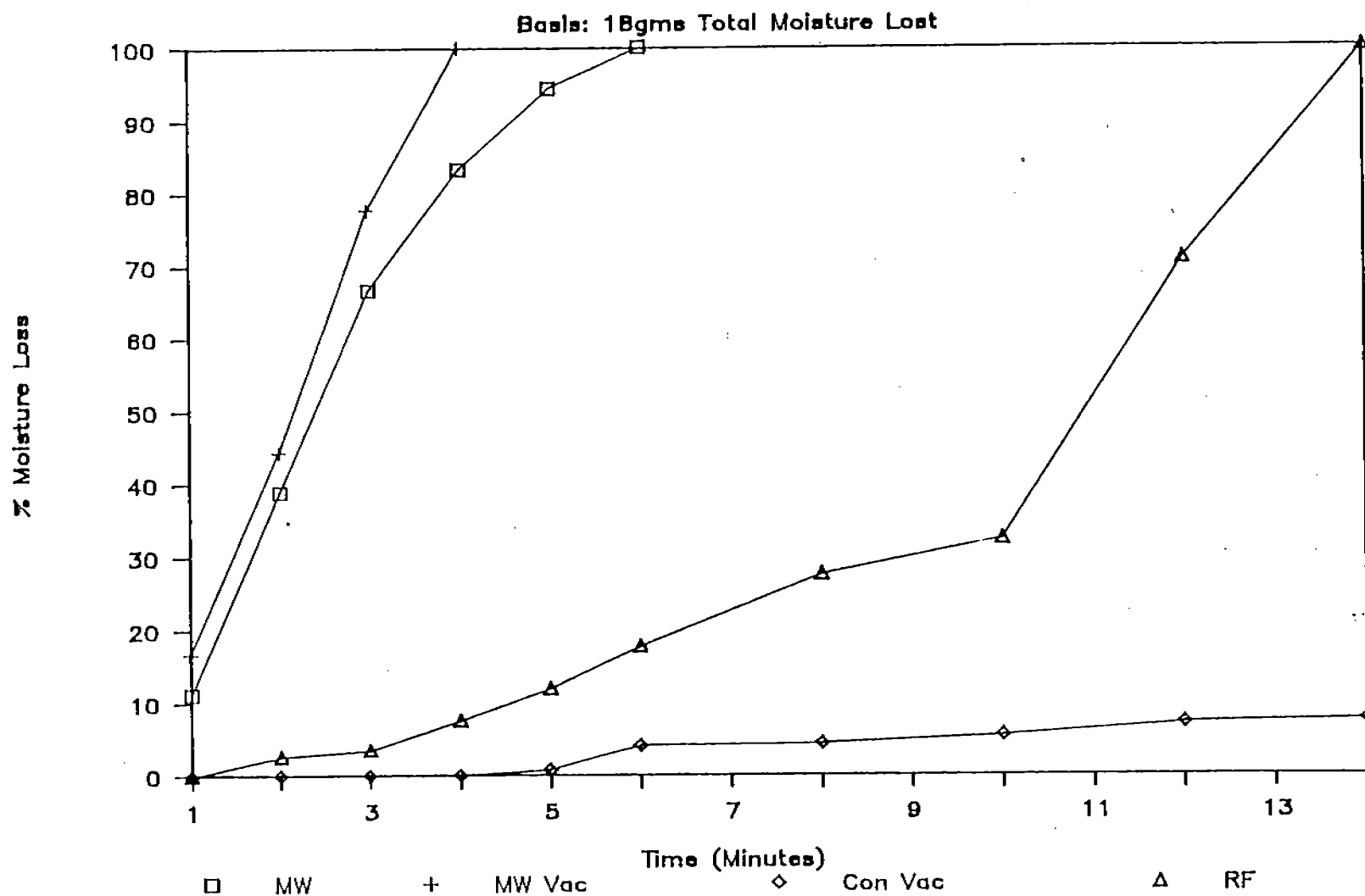
Acid Recovery Research

Adsorption--Pilot-scale adsorption tests were conducted at the University of Missouri-Rolla using an adsorption unit with a 100-g/cycle sugar capacity. Synthetic solutions were used initially to determine carbon-loading, void volume, liquid retention, and pressure-flow profiles. Adsorption and desorption capacities measured (100 g sugar adsorbed/kg carbon) corresponded to those measured in the small-scale (3 g/cycle) columns. Actual hydrolyzate feeds were evaluated through 38 cycles using the pilot-scale system. During the initial 9 to 11 cycles, the adsorption capacity decreased to 82 percent of the value observed in the small columns and remained relatively constant for the remaining cycles. Hot ethanol was used successfully to remove the sugars from the column (Sitton and Book 1987).

Solvent Extraction--A computer program has been developed to compare the extraction capabilities of various solvents and to optimize parameters.

FIGURE 1

Percent Moisture Loss vs Time (Minutes)



Equilibrium data has been collected for 7 solvents. A laboratory Karr extraction column was used to demonstrate the capabilities of the extraction program. Three experimental runs were conducted at solvent-to-feed ratios of 1:1, and three runs were conducted at solvent-to-feed ratios of 3:1. The feed composition of the hydrolyzate solution at both ratios was 50-wt percent H_2SO_4 , 10-wt percent glucose, and 40-wt percent water. The amount of H_2SO_4 recovered in the extract ranged from 73 to 83 percent, nearly independent of the solvent-to-feed ratio. The amount of glucose recovered in the raffinate ranged from 35 to 91 percent with the higher recovery rates found at the 3:1 solvent-to-feed ratio (Clausen and Gaddy 1987).

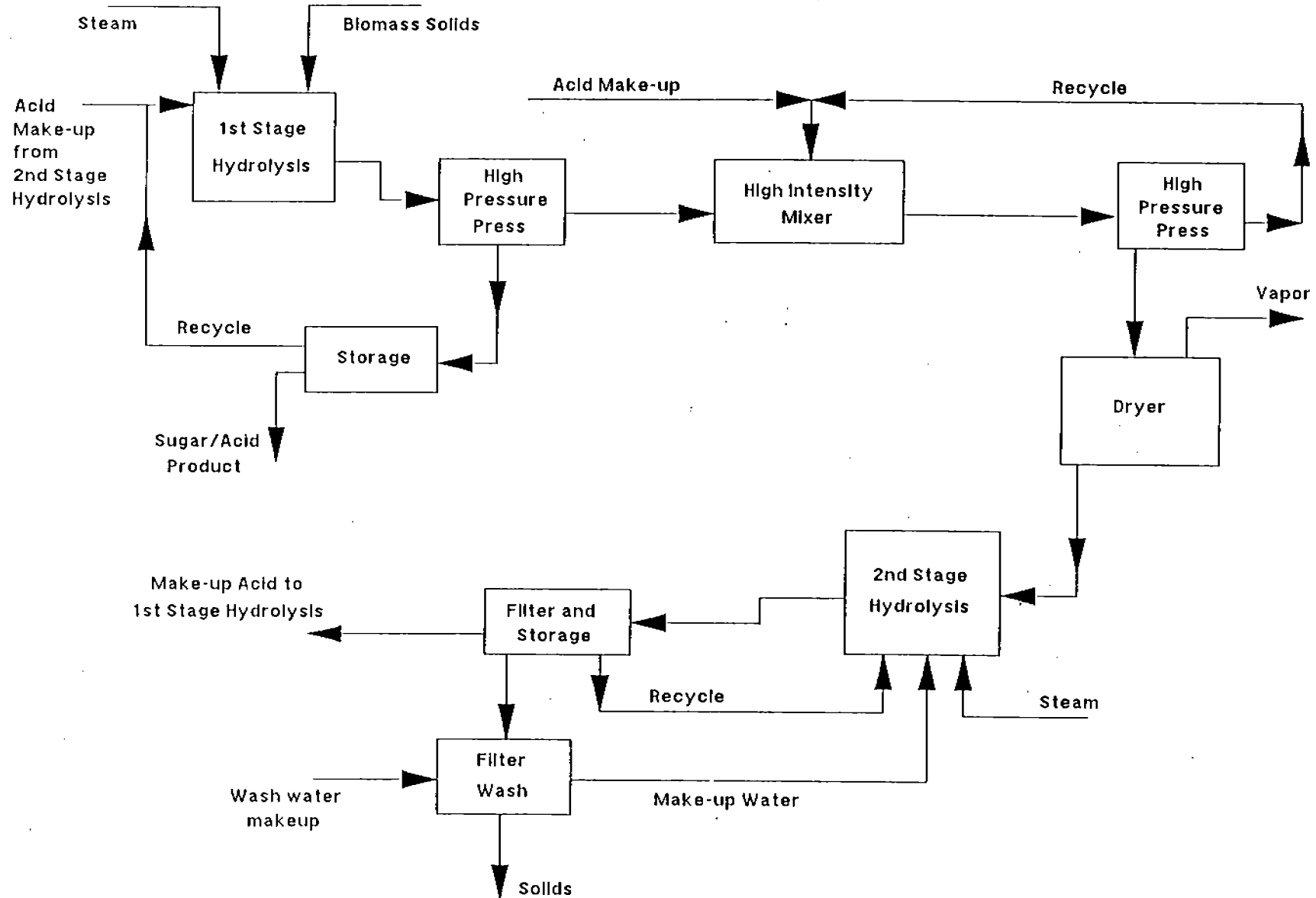
Ion Exchange--Preliminary ion exchange research is being conducted to screen commercial resins for their potential use in recovering sulfuric acid. Initial studies indicate that a strongly-acidic cation exchanger resin of the "GEL" type Amberlite IR 120 PLUS sulfonic acid functionality may be the appropriate resin for acid/sugar separation (Hester and Nanguneri 1987).

DISCUSSION

Considerable progress has been made through research and development activities conducted in the areas of acid hydrolysis and acid recovery. Based on the results of acid hydrolysis research, an improved process design has been developed. The flow diagram of the process is shown in Figure 2. Corn stover ground to 1/8 in. is hydrolyzed in 5-percent acid at 212°F for 2 hours. High-pressure pressing is used to dewater the mixture. The hydrolyzate is recycled back for processing of subsequent batches of raw stover which increases the xylose concentration of this stream. The solids from the first stage are mixed with 25-percent acid using a high-intensity mixer. High-pressure pressing is again used to dewater the mixture. The solids are then fed to a radio-frequency-assisted vacuum dryer where water is removed to concentrate the acid to 70 percent (aqueous phase). Cellulose hydrolysis takes place in 10-percent acid at 100°C for 4 hours. The resulting cellulose hydrolyzate is recycled to the first stage to be used as makeup acid. This improved process design reduces energy requirements by 30 percent and retention times by 20 percent. Equipment requirements also have been reduced, resulting in a more efficient, streamlined process.

Advances made in acid recovery research during the past year have the potential to significantly increase the economic feasibility of the acid hydrolysis processing system. Extraction of sulfuric acid for recycle back to the process has been successfully proven in laboratory studies at the University of Arkansas. Recycle of acid will allow for the use of higher acid concentrations in the process, resulting in higher sugar yields at shorter retention times. Adsorption technology, successfully demonstrated at the University of Missouri-Rolla, results in the production of crystalline sugar which can be diluted to any concentration suitable for optimum fermentation. The resulting acid solution can be recycled. Preliminary ion exchange results also show the potential of this technology for recovering sulfuric acid.

FIGURE 2



2 stage Concentrated Sulfuric Acid Hydrolysis - Flow Diagram

FURTHER WORK

Acid hydrolysis optimization research will continue to evaluate equipment and define process conditions for optimum process operation. Laboratory- and bench-scale tests designed to lower acid requirements while maintaining high yields will be conducted. Evaluations of alternative equipment to improve the dispersion of acid throughout the stover will continue in an effort to reduce acid requirements. Acid recovery research of the extraction process will focus on the optimization of process conditions based on using one solvent. Pilot-scale adsorption studies will be conducted to determine the kinetics of the adsorption-desorption process. Column dynamics and resin performance will be evaluated in ion exchange studies.

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ACID RECOVERY OF POLYAMINE

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ABSTRACT

Acid hydrolysis of cellulosics will result in solutions of glucose and xylose contaminated by the acid. Neutralization with lime will remove most of the sulfuric acid in the form of precipitated gypsum but a sufficient amount of calcium ions will remain in the solution. The calcium ions are inhibitory towards xylose isomerase enzyme which is sometimes employed to convert xylose to xylulose to be fermented to ethanol. Removal of the acid catalysts by a solid resin adsorbent will therefore help to avoid this problem of inhibition. A class of polymers (PA-polyamine) have been used to remove acids from the sugar solution.

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